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The Alkylation of Naphthalene over One-Dimensional Fourteen-Membered Ring Zeolites. The Influence of Zeolite Structure and Alkylating Agent on the Selectivity for Dialkylnaphthalenes

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The alkylation, i.e., isopropylation, *s*-butylation, and *t*-butylation, of naphthalene (NP) was examined over one-dimensional fourteen-membered (14-MR) zeolites: CIT-5 (CFI), UTD-1 (DON), and SSZ-53 (SFH), and compared to the results over H-mordenite (MOR) to elucidate how zeolite structure and alkylating agent play roles in the shape-selective catalysis. The β,β-selectivities (for β,β-dialkylnaphthalene (2,6- and 2,7-dialkylnaphthalenes, β,β-DAN)) and the 2,6-selectivities (for 2,6-DAN) were varied with the types of zeolite and of alkylating agent. MOR gave high β,β-selectivities in the all alkylations in the range of 150–300 °C. However, the 14-MR zeolites, CFI, DON, and SFH, gave much lower β,β-selectivities in the isopropylation: bulky and less stable α,β- and α,α-diisopropylnaphthalenes (α,β-DIPN: 1,3-, 1,5-, and 1,7-DIPN); α,α-DIPN (1,4- and 1,5-DIPN) were predominantly obtained under kinetic control at low temperatures, and stable and less bulky β,β-DIPN were formed under thermodynamic control at high temperatures. The β,β-selectivities were higher than 95% over CFI in the *s*-butylation, and increased from 50–60% at 150 °C to 75% at 300 °C over DON and SFH, respectively. They were almost 100% in the *t*-butylation over all zeolites. The alkylation over MOR occurred with high 2,6-selectivities in the range of 150–250 °C: 60% for the isopropylation, 80% for the *s*-butylation, and 95% for the *t*-butylation. CFI, DON, and SFH gave the 2,6-selectivities in the range of 5–30% in the isopropylation, 65%, 55%, and 50%, respectively, in the *s*-butylation, and higher than 80% in the *t*-butylation. These different features are explained by the discrimination of the least bulky DAN isomers from the other isomers by steric restriction with the zeolite channels at the transition states: β,β-DAN from the DAN isomers, and 2,6-DAN from β,β-DAN. The bulkiness of alkylating agent also enhances the discrimination of the isomers, particularly, between 2,6- and 2,7-DAN. The β,β- and 2,6-selectivities are synergistically governed by the zeolite channel and the bulkiness of alkylating agents.

Shape-selective catalyses occur by differentiating reactants, products, and/or reaction intermediates according to their shape and size in sterically restricted environments of microporous crystals.[1–8] The selectivities for products are determined by molecular size and configuration of the pore-entrance and channel, as well as by the characteristics of its catalytic center. Only a reactant molecule, whose dimension is less than a critical size, can enter into the pore and react at the catalytic site. Furthermore, only product molecules which can diffuse out through the pores, will appear in the product.

The selectivity for product isomers is determined by the discrimination of the least bulky isomers with the channels at the transition states in the alkylation of aromatics: this is so called "restricted transition-state selectivity" as discussed in previous papers.[1] In this mechanism, fitting the transition state of the least bulky isomer to zeolite channels is an important key for highly shape-selective catalyses. There are also two other mechanisms: "reactant selectivity" by the discrimination of the bulkiness of reactants to enter the zeolite and "products selectivity" by preferential diffusion from the zeolite.[1] However, if the channels are large enough to allow the transition state of bulky isomers in the channels, the catalyses are governed by kinetic and/or thermodynamic controls to yield predominantly bulky isomers at low temperatures, and to yield thermodynamically stable isomers with increasing temperature. These considerations indicate that the discrimination of bulky molecules from the channels is one of the key factors for shape-selective catalysis by zeolites, and that it depends on the types of zeolite and alkylating agent.

The isopropylation of polynuclear hydrocarbons, such as naphthalene (NP) and biphenyl (BP) is a typical acid-catalyzed reaction for demonstrating the shape-selective nature of zeolites.[4–15] Selective formation of the least bulky 2,6-diisopropylnaphthalene (2,6-DIPN) and 4,4′-diisopropylbiphenyl (4,4′-DIPB) is facilitated over zeolites if catalytic sites are sterically restricted in the channels. In previous papers, we and other workers described that 2,6-DIPN was selectively produced from NP over dealuminated H-mordenite (MOR).[9–15] Catalytically active sites in MOR channels effectively exclude the transition state of bulky DIPN isomers in the isopropylation, thus resulting in selective formation of the least bulky 2,6-DIPN.[9] These results prompted us to study how the difference in dimensionality, pore size, and channel structures of zeolite are related to the catalysis, and how the bulkiness of alkylating agent influences the transition states to lead to the shape-selective catalysis in zeolite channels. In previous pa-

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Table 1. Properties of Zeolites

Zeolite	Topology (FTC)	Pore entrance (MR)	Channel structure	Cage[a)] (MR)	Pore entrance /nm^2	SiO$_2$ /Al$_2$O$_3$	Surface area /m^2 g^{-1}	External surface area[b)] /m^2 g^{-1}	Pore volume /mL g^{-1}	NH$_3$ peak temperature /°C	Acid amount /mmol g^{-1}
Mordenite	MOR	12	Straight with 8-MR channels	—	0.67 × 0.72	128	460	35	0.16	389	0.20
CIT-5	CFI	14	Slightly corrugated	16	0.72 × 0.75	160	339	38	0.14	294	0.13
UTD-1	DON	14	Straight	—	0.70 × 0.95	200	403	15	0.16	288	0.12
SSZ-53	SFH	14	Largely corrugated	22	0.65 × 0.88	64	385	83	0.11	316	0.26

a) The member of the cages of the zeolites is the maximum size of oxygen rings estimated from data in the reference.[26] b) Calculated from *t*-plot of N_2 adsorption.

pers, we discussed the alkylation of NP over one-dimensional 12-MR zeolites, MOR, SSZ-24 (AFI), SSZ-55 (ATS), and SSZ-42 (IFR), and three-dimensional 12-MR zeolites,[16] Y-(FAU), β-(BEA), and CIT-1 (CON) zeolites by using propene, 1-butene, and 2-methylpropene as alkylating agent,[17] and proposed that a controlling factor for shape-selective formation of β,β-dialkylnaphthalenes (β,β-DAN) and 2,6-DAN is steric restriction of the transition state by zeolite channels.

In this paper, we describe the alkylation, i.e., isopropylation, *s*-butylation, and *t*-butylation of NP, over some recently found one-dimensional 14-MR zeolites, CIT-5 (CFI) with slightly corrugated (almost straight) channels, UTD-1 (DON) with straight channels, and SSZ-53 (SFH) with largely corrugated channels,[18–25] and compared the formation of dialkylnaphthalenes (DAN) to MOR with straight 12-MR channels. The discussion in this paper is based on the β,β-selectivity (selectivity for β,β-DAN (2,6- and 2,7-DAN)) and the 2,6-selectivity (selectivity for 2,6-DAN) among the DAN isomers in order to focus key factors for controlling the catalysis in sterically restricted environments of zeolites. The abbreviation of zeolites is expressed by Framework Type Code (FTC) from the IZA Structure Commission.[26] Features on catalytic activities are shown in Supporting Information.

Experimental

Zeolites. CFI, DON, and SFH were synthesized according to the literature.[20,22,24] MOR was obtained from Tosoh Corporation ($SiO_2/Al_2O_3 = 128$; TSZ-690HOA). All zeolites were used as H^+-form in catalytic alkylation of NP. Table 1 shows typical properties of zeolites related to the catalysis. Other results on the characterization of the zeolites used in this work are shown in our previous paper.[27]

The Alkylation of NP. The alkylation of NP was carried out in a 100-mL SUS-316 autoclave as described in our previous papers.[16,17] Typical conditions of the isopropylation are: NP 6.42 g (50 mmol), catalyst 0.25 g, reaction temperature 150–300 °C, and reaction period 4 h under propene pressure of 0.8 MPa (0.4 MPa for 1-butene in the *s*-butylation and for 2-methylpropene in the *t*-butylation). An autoclave containing NP and the catalyst was flushed with nitrogen before heating. After reaching the reaction temperature, propene was introduced to the autoclave, and the reaction was started with agitation. The pressure was kept constant throughout the reaction. After cooling the autoclave, the catalyst was filtered off, and washed well with toluene. Liquid bulk products were analyzed by using a Gas Chromatograph GC-14A (Shimadzu Corporation) equipped with TC-17 (25 m × 0.25 mm; film thickness: 0.25 µm; GL Sciences) and/or HP-INNOWax (60 m × 0.25 mm; film thickness: 0.5 µm; Agilent Technologies) capillary columns. The products were also identified by using a Gas Chromatograph-Mass Spectrometer GC-MS 5000 (Shimadzu Corporation) by using the above columns.

The yields of alkylnaphthalene (AN) and dialkylnaphthalene (DAN) isomers of each product are calculated on the basis of the amount of starting NP, and the selectivities for each DAN isomer are expressed based on total amounts of DAN isomers.

DAN in isopropylation, *s*-butylation, and *t*-butylation is defined as DIPN, DSBN, and DTBN, respectively. β,β-DAN is defined as a mixture of 2,6- and 2,7-DAN, α,β-DAN as 1,3-, 1,6-, and 1,7-DAN, and α,α-DAN as 1,4- and 1,5-DAN. The β,β-, α,β-, and α,α-selectivities are defined as the selectivities for β,β-, α,β-, and α,α-DAN among DAN isomers, respectively. The 2,6- and 2,7-selectivities are the selectivities for 2,6- and 2,7-DAN among DAN isomers, respectively.

The catalytic activities based on the yield of alkylated products are shown in Figures S1–S6 in Supporting Information.

Results and Discussion

The Isopropylation. The isopropylation of NP over MOR, CFI, DON, and SFH gave mixtures of isopropylnaphthalenes (IPN), diisopropylnaphthalenes (DIPN), and triisopropylnaphthalenes (TriIPN). Catalytic activities increased with temperature; however, the conversion decreased at higher temperatures in some cases. The decrease in conversion was accompanied by a decrease in yield of DIPN and an increase in the yield of IPN: this is due to de-alkylation of DIPN and IPN (see Figures S1 and S2 in Supporting Information).

The influence of reaction temperature on the selectivities for DIPN isomers in the isopropylation of NP is shown in Figure 1 over MOR and CFI, and in Figure 2 over DON and SFH. The products consisted of β,β-, α,β-, and α,α-DIPN isomers over these zeolites, and they varied with the type of zeolite. The β,β-selectivities were over 80–85% in the range of 150–300 °C in the isopropylation over MOR: the α,β- and α,α-selectivities were less than 20%. However, the 14-MR zeolites, CFI, DON, and SFH, gave much lower β,β-selectivities than MOR. The β,β-selectivities over CFI gradually increased with the increase in reaction temperature from 35% at 150 °C to 65% at 275–300 °C, accompanying the decrease in the α,β-

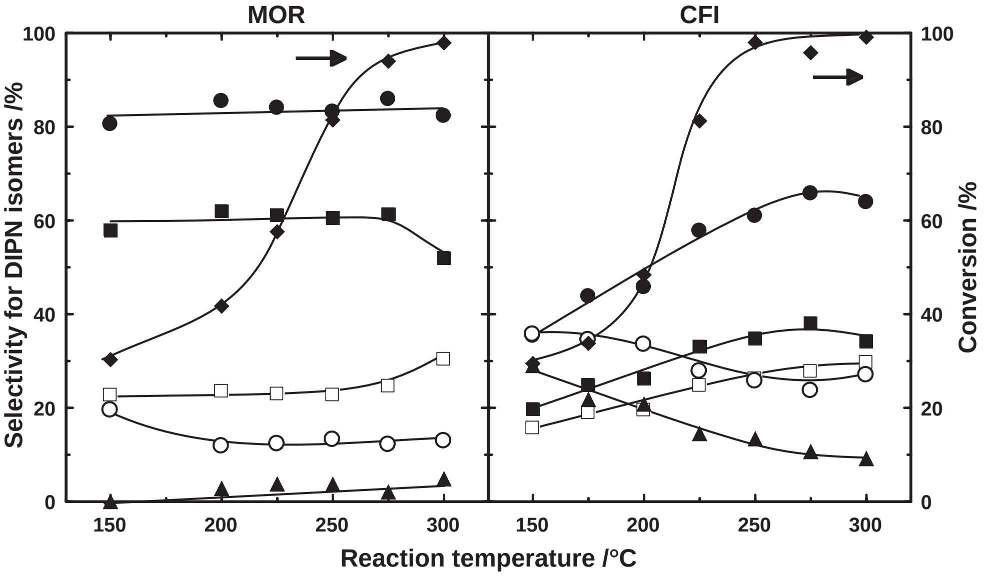

Figure 1. The influence of reaction temperature on the selectivity for DIPN isomers in the isopropylation of NP over MOR and CFI. Reaction conditions: NP, 50 mmol; catalyst, 0.25 g; temperature, 150–300 °C; propene pressure, 0.8 MPa; period, 4 h. Legends: ◆: conversion; ■: 2,6-DIPN; □: 2,7-DIPN; ●: β,β-DIPN; ○: α,β-DIPN; ▲: α,α-DIPN.

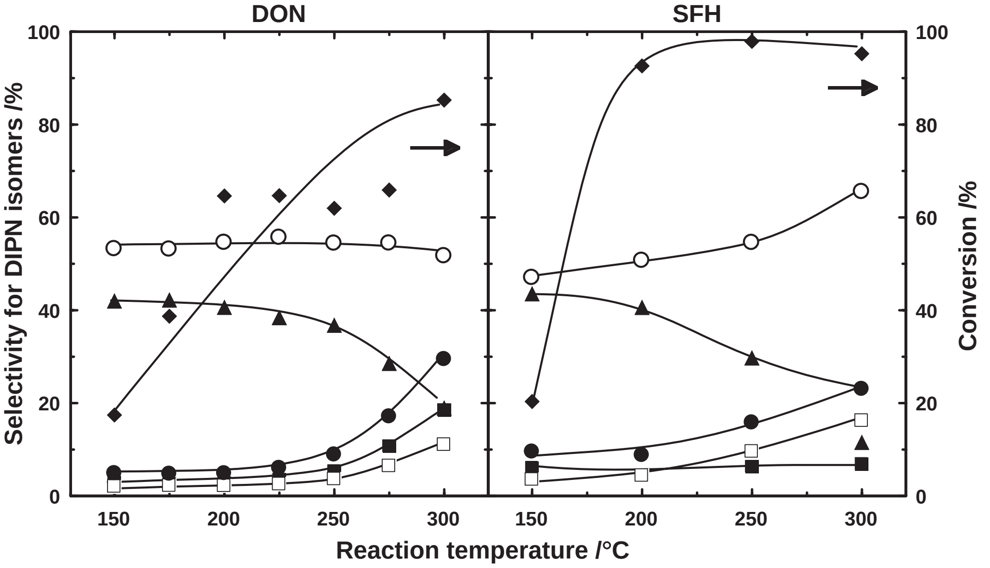

Figure 2. The influence of reaction temperature on the selectivity for DIPN isomers in the isopropylation of NP over DON and SFH. Reaction conditions: NP, 50 mmol; catalyst, 0.25 g (DON); NP, 20 mmol; catalyst, 0.1 g (SFH). Other conditions and legends: see Figure 1.

and α,α-selectivities. Principal products over DON and SFH were α,β- and α,α-DIPN, particularly at lower temperatures; however, the β,β-selectivities increased with increase in temperature: 5% at 150 °C and 35% at 300 °C for DON and 10% at 150 °C to 25% for SFH at 300 °C The α,α-selectivities decreased with increase in temperature over DON and SFH; however, the α,β-selectivities remained constant for DON, and increased for SFH.

The 2,6-selectivities in the isopropylation varied with the zeolites similarly to β,β-selectivities. The 2,6- and 2,7-selectivities over MOR were around 60% and 20% at low and moderate temperatures below 275 °C, respectively, although some decreases in 2,6-selectivities and increases in 2,7-selectivities occurred at 300 °C. However, the 2,6-selectivities over the 14-MR zeolites were also much lower than those over MOR. The 2,6-selectivities for CFI, DON, and SFH were 20%, 5%, and 10% at 150 °C, and they increased to 40%, 30%, and 25% at 300 °C, respectively.

These results show that the mechanisms of the isopropylation are different by the type of zeolites, MOR, CFI, DON, and SFH. MOR was shape selective for the formation of β,β-DIPN; however, the 14-MR zeolites were not. These differences are due to steric interaction of DIPN isomers in the channels, which are invoked by the difference in structures, such as pore entrance and channel—MOR: 12-MR pore entrance (0.67 nm × 0.72 nm) with straight channels; CFI: 14-

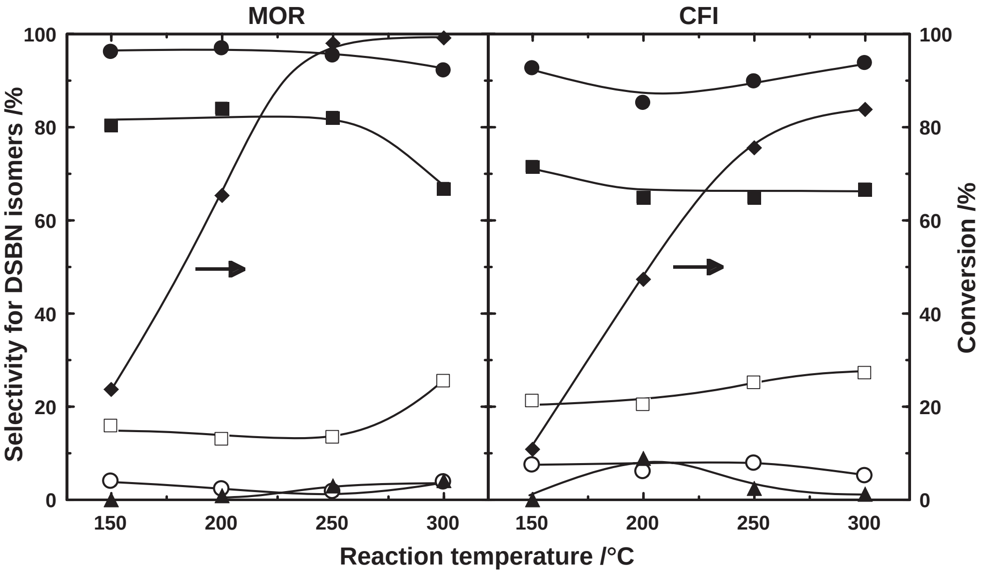

Figure 3. The influence of reaction temperature on the selectivity for DSBN isomers in the *s*-butylation of NP over MOR and CFI. Reaction conditions: NP, 50 mmol; catalyst, 0.25 g (MOR); NP, 25 mmol; catalyst, 0.125 g (CFI); temperature, 150–300 °C; 1-butene pressure, 0.5 MPa; period, 4 h. Legends: ◆: conversion. ■: 2,6-DSBN; □: 2,7-DSBN; ●: β,β-DSBN; ○: α,β-DSBN; ▲: α,α-DSBN.

MR pore entrance (0.72 nm × 0.75 nm) and slightly corrugated (almost straight) channel with 16-MR cages, DON: 14-MR pore entrance (0.74 nm × 0.95 nm) with straight channel, and SFH: 14-MR pore entrance (0.65 nm × 0.88 nm) and corrugated channel with 22-MR cages.[26,28] Consequently, the reaction space in zeolites is in the order: MOR < CFI ≪ DON < SFH, and steric restriction in the catalysis increases in the reverse order. MOR pores are small enough to discriminate the less bulky β,β-DIPN from other bulky isomers. However, steric restriction of the channels of 14-MR zeolites is too loose for shape-selective isopropylation, resulting in the operation of kinetic and thermodynamic controls. Kinetic control is predominant at lower temperatures, i.e., a nucleophilic attack of isopropyl cation to the electron-rich α-carbon of NP leads to predominant formation of α,α- and α,β-DIPN. Thermodynamic control also operates in the reaction with increase in temperature, resulting in the predominant formation of less bulky and stable β,β-DIPN.

The 2,6-selectivities also gave the discrimination of 2,6-DIPN from other bulky isomers, particularly, between 2,6- and 2,7-DIPN. The difference in steric interaction with the channels between 2,6- and 2,7-DIPN was invoked by the difference in the bulkiness between two isomers. The high 2,6-selectivities only appeared in the isopropylation over MOR, and 14-MR zeolites, CFI, DON, and SFH, gave lower 2,6-selectivities. These results mean that CFI, DON, and SFH cannot discriminate 2,6- and 2,7-DIPN from other bulky isomers although MOR can discriminate 2,6- and 2,7-DIPN as previously discussed.[10]

The 2,6-selectivities decreased over MOR at high temperatures, accompanying the increase in the 2,7-selectivities; however, the β,β-selectivities remained almost constant. This is due to the isomerization of 2,6-DIPN to 2,7-DIPN because the equilibrium mixture contains almost equal amounts of 2,6- and 2,7-DIPN.[17] The isomerization occurs at external acid sites because the selectivity for 2,6-DIPN in encapsulated products maintained at around 70% even at 325 °C (data not shown).

The *s*-Butylation. The influence of reaction temperature on the *s*-butylation of NP over CFI, DON, and SFH was examined in order to know the influence of the bulkiness of alkylating agent on the catalysis, and compared to the results of MOR. Similar catalytic activities in the *s*-butylation were observed as in the isopropylation: *s*-butylnaphthalenes (SBN) and di-*s*-butylnaphthalenes (DSBN) were obtained as principal products with small amounts of tri-*s*-butylnaphthalenes (TriIPN) (see Figures S3 and S4 in Supporting Information).

Figures 3 and 4 show the influence of reaction temperature on the selectivities for DSBN isomers over MOR, CFI, DON, and SFH. The β,β-selectivities were higher than 90% for MOR and CFI. However, the β,β-selectivities over DON and SFH were lower than those over MOR and CFI. They increased gradually with increase in temperature: 50% at 150 °C to 75% at 300 °C for DON and 60% at 150 °C to 75% for SFH at 300 °C. The increase in the β,β-selectivities accompanied the decrease in the α,β-selectivities. These results mean that MOR and CFI can discriminate effectively β,β-DSBN from other bulky α,α- and α,β-DSBN isomers by steric interaction with the channels at their transition states. DON and SFH have also some shape-selective nature for the formation of β,β-DSBN; however, kinetic control also predominantly operates at lower temperatures, and the contribution of thermodynamic control increases with increase in temperature.

The higher β,β-selectivities in the *s*-butylation compared to the isopropylation are invoked by the difference in the bulkiness of isopropyl and *s*-butyl moieties in DAN isomers. The differences in the interaction of β,β-DSBN with the channels are enhanced much compared to those of β,β-DIPN. Although molecular diameters of β,β-DSBN are almost the same as those of β,β-DIPN, the replacement of isopropyl moieties with *s*-butyl ones will enhance the difference in the bulkiness of

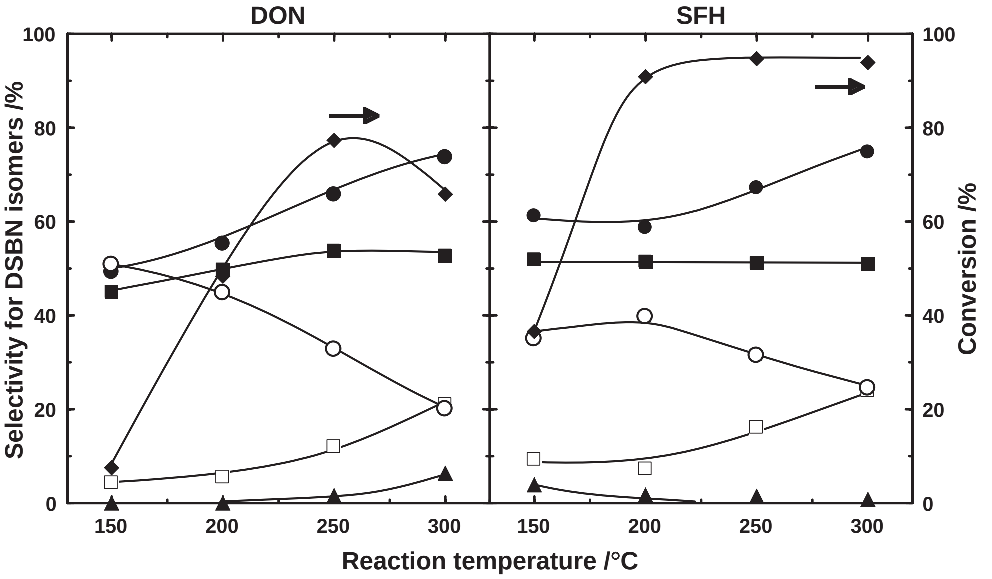

Figure 4. The influence of reaction temperature on the selectivity for DSBN isomers in the *s*-butylation of NP over DON and SFH. Reaction conditions: NP, 25 mmol; catalyst, 0.125 g. Other conditions and legends: see Figure 4.

β,β-DSBN from other bulky α,α- and α,β-DSBN in zeolite channels. These differences enhance selective formation of β,β-DSBN over these zeolites by the replacement of isopropyl moieties with *s*-butyl ones. Thus, α,β- and α,α-DSBN in the *s*-butylation are more easily excluded from the channels than α,β- and α,α-DIPN in the isopropylation. These differences in the channels may result in higher β,β-selectivities in the *s*-butylation.

The 2,6-selectivities were also around 70–80% among their isomers in the *s*-butylation over MOR and CFI as shown in Figure 3. However, they were around 45–55% in the range of 150–300 °C over DON and SFH as shown in Figure 4. The 2,7-selectivities were 5% for DON and 10% for SFH at 150 °C; however, increased to 20% and 25%, respectively at 300 °C. These results mean that channels of MOR and CFI can discriminate the difference in the size of 2,6- and 2,7-DSBN. DON and SFH have some shape-selective nature in the *s*-butylation at low temperatures, although kinetic control also operates. However, thermodynamic control enhanced 2,7-selectivities with increase in temperature although the 2,6-selectivities were almost constant. *s*-Butyl moieties in DSBN isomers invoke the differences between 2,6- and other isomers, particularly between 2,6- and 2,7-DSBN, in steric restriction with the channels of all zeolites, similarly to the discussion on β,β-selectivities.

The 2,6-selectivities decreased at 300 °C in the *s*-butylation over MOR; however, the β,β-selectivities remained almost constant. This is due to the isomerization of 2,6-DSBN to 2,7-DSBN at external acid sites similarly to the isomerization of 2,6-DIPN in the isopropylation.

The *t*-Butylation. Steric restriction among DAN isomers by zeolite channels is enhanced by the bulkiness of alkylating agents as discussed in the isopropylation and *s*-butylation. It is interesting to know the influence of bulky alkylating agent, 2-methylpropene on the selectivity for DTBN isomers in the alkylation of NP. The *t*-butylation gave *t*-butylnaphthalenes (TBN) and di-*t*-butylnaphthalenes (DTBN) with a small amount of tri-*t*-butylnaphthalenes (TriTBN). However, catalytic activities were lower than that of the *s*-butylation and isopropylation although they increased with temperature (see Figures S5 and S6 in Supporting Information).

The β,β-selectivities were higher than 95% over MOR, CFI, DON, and SFH in the range of 150–300 °C in the *t*-butylation as shown in Figures 5 and 6. These results mean that these zeolites have channels small enough for the discrimination of β,β-DTBN from other DTBN isomers. The high 2,6-selectivities were also observed over all zeolites. The 2,6-selectivities were higher than 95% over MOR at low and moderate temperatures although they decreased to 60% at 300 °C. The 2,6-selectivities at 250 °C were higher than 90% over MOR and CFI; however, they were around 80% for DON and SFH. These results indicate that the discrimination of 2,6- and 2,7-DTBN by the channels of DON and SFH is looser than that by MOR and CFI. The differences are due to structural differences in channels of the zeolites. Reaction spaces in DON and SFH are too large for exclusive formation of 2,6-DTBN.

The 2,6-selectivities also decreased at 300 °C in the *t*-butylation of NP over MOR, CFI, and SFH accompanying the increase in the 2,7-selectivities; however, the β,β-selectivities almost stayed constant. The decrease in the 2,6-selectivities is due to the isomerization of 2,6-DTBN to 2,7-DTBN at the external acid sites similarly to the isomerization of 2,6-DIPN in the isopropylation and of 2,6-DSBN in the *s*-butylation.

Shape-Selective Catalysis of the 14-MR Zeolites in the Alkylation of NP. Catalytic performances of zeolites for shape-selective catalysis are generally influenced by many factors.[1,2] Some typical factors of zeolites are pore-entrance, channel, and physical properties, such as crystal size, morphology, and density and distribution of active species, which are also influenced by preparation and post-synthesis methods. Reaction conditions, such as temperature, pressure, period, and catalyst amount, also influence catalytic performances. Among these factors, pore-entrance and channel structures are the

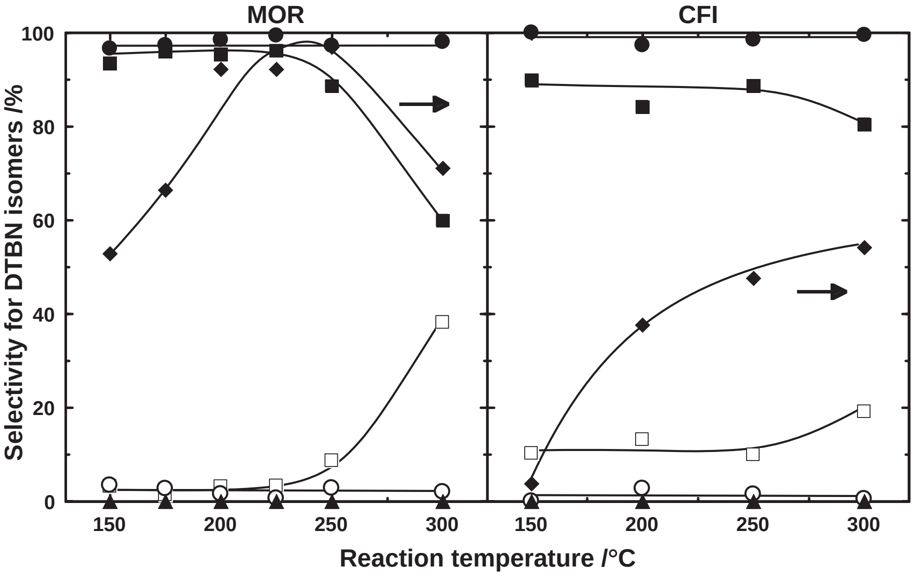

Figure 5. The influence of reaction temperature on the selectivity for DTBN isomers in the *t*-butylation of NP over MOR and CFI. Reaction conditions: NP, 50 mmol; catalyst, 0.25 mg (MOR); NP, 25 mmol; catalyst, 0.125 mg (CFI); temperature, 150–300 °C; 2-methylpropene pressure, 0.5 MPa; period, 4 h. Legends: ◆: conversion; ■: 2,6-DTBN; □: 2,7-DTBN; ●: β,β-DTBN; ○: α,β-DTBN; ▲: α,α-DTBN.

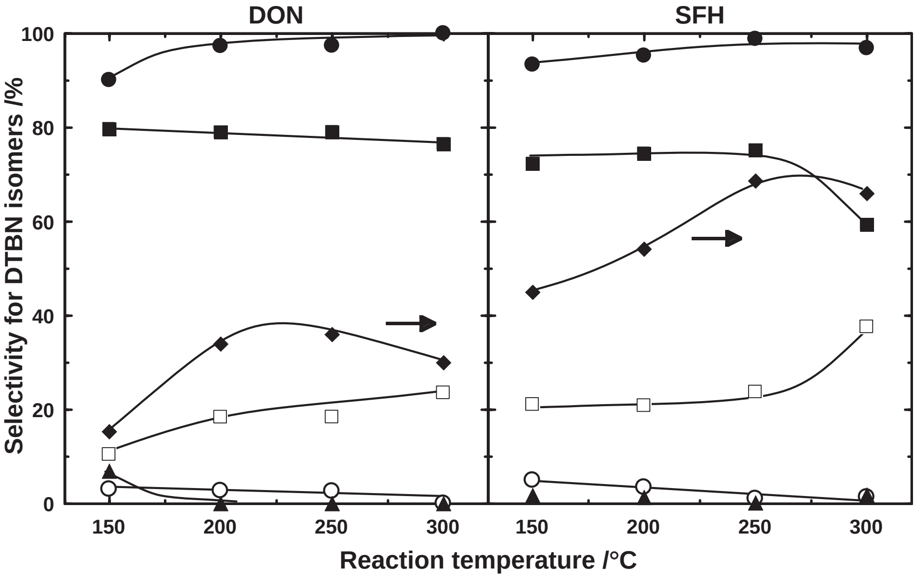

Figure 6. The influence of reaction temperature on the selectivity for DTBN isomers in the *t*-butylation of NP over DON and SFH. Reaction conditions: NP, 25 mmol; catalyst, 0.125 g. Other conditions and legends: see Figure 5.

most important keys for controlling shape-selectivity in the catalysis.[1,2]

There are two types of selectivities for DAN isomers in the alkylation of NP: β,β-selectivities and 2,6-selectivities. The β,β-selectivities are due to discrimination of less bulky β,β-DAN from bulkier α,α- and α,β-DAN because sizes of DAN isomers decrease in the order: α,α-DAN > α,β-DAN > β,β-DAN. The α,α- and α,β-selectivities are an index for the bulky isomers formed principally under kinetic control. The high β,β-selectivities also appeared for stable isomers under thermodynamic control, which work particularly at higher temperatures under sterically less restricted reaction environments: the 2,7-DAN/2,6-DAN ratio should approach unity because of thermodynamic equilibrium.[29]

The 2,6-selectivities are due to the discrimination of the least bulky 2,6-DAN from its DAN isomers, particularly, between 2,6- and 2,7-DAN, because 2,7-DAN is slightly bulkier than 2,6-DAN. If the channels are small enough to exclude bulky isomers by steric limitation of transition states in the channels, shape selective catalysis occurs to yield less bulky isomers. However, shape-selective catalysis will not occur if the channels are large enough for the formation of transition states for bulkier isomers.

The differences in zeolite structures, particularly, pore-en-

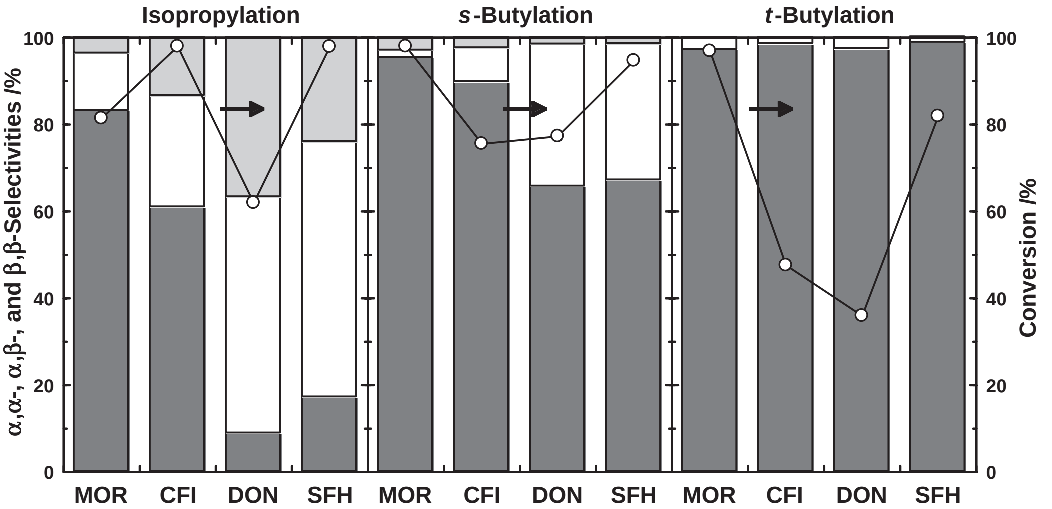

Figure 7. The selectivities for DAN isomers in the alkylation of NP over the zeolites. Reaction conditions: temperature, 250 °C. Other conditions: see Figures 1–6. Legends: ■: *β*,*β*-DAN; □: *α*,*β*-DAN; ▨: *α*,*α*-DAN; ○: conversion.

trance and channel also influence the shape-selective nature in the alkylation as discussed above. The size of pore-entrance of the zeolites in this study increases in the order: MOR < CFI ≪ SFH < DOH.[26] However, they have different types of channels: straight channels for MOR and DON, and corrugated channels with 16-MR cage for CFI, which are almost straight only with small corrugation, and corrugated channels with 22-MR cage for SFH (see Figure S7 in Supporting Information).[28] These differences suggest that reaction space in zeolite channels is in the order: MOR < CFI ≪ DON ≪ SFH, and steric interaction during the catalysis decreases in the reverse order.

Figure 7 shows the influence of the types of zeolite and alkylating agent on the *β*,*β*-selectivities in the alkylation of NP at 250 °C. These are typical selectivities of the zeolites for DAN isomers in the alkylation of NP because DAN isomers were not significantly isomerized under reaction conditions at 250 °C.

The *β*,*β*-selectivities highly depend on the types of zeolite and alkylating agent. They were enhanced by the bulkiness of alkylating agents for all zeolites in this study. However, they were also influenced by reaction space originating from channel structures. Among zeolites, MOR was the most shape selective for all alkylating agents in this study. MOR channels most effectively fit the transition states of the least bulky *β*,*β*-DIPN, and they effectively exclude the formation of other bulky isomers. Among 14-MR zeolites, CFI gave higher *β*,*β*-selectivities even in the isopropylation; however, DON and SFH were not shape selective because their channels are too large for the discrimination of *β*,*β*-DIPN from other bulky isomers. Kinetic and/or thermodynamic controls are key factors for the isopropylation over DON and SFH as discussed in previous sections. The increase in the *β*,*β*-selectivities in the *s*-butylation and *t*-butylation were also observed for 14-MR one-dimensional zeolites, CFI, DON, and SFH as well as for MOR. These results mean that shape-selective nature appears over the 14-MR zeolites in the *s*-butylation, and these zeolites are highly shape-selective in the *t*-butylation. The replacement of isopropyl moieties with bulky *s*-butyl and *t*-butyl ones in DAN isomers invokes the difference in the bulkiness of *β*,*β*-DAN from other isomers, because the replacement of bulky alkyl groups increases steric interaction of the DAN isomers with the channels. Particularly, the difference of the bulkiness between *β*,*β*- and *α*,*β*-DSBN in the *s*-butylation enhances the discrimination of less bulky *β*,*β*-DSBN isomers in the zeolite channels although effective molecular diameters of *β*,*β*-DSBN are almost the same as that of *β*,*β*-DIPN. *t*-Butyl moieties in the DTBN isomers also enhance the *β*,*β*-selectivities in the *t*-butylation. Thus, *α*,*α*- and *α*,*β*-DTBN are effectively excluded from the channels by the increase in the bulkiness of alkylating agents in the order: isopropylation < *s*-butylation < *t*-butylation.

Figure 8 shows the influence of the type of zeolite and alkylating agent on the 2,6-selectivities at 250 °C. Similar changes of 2,6-selectivities were observed for *β*,*β*-selectivities over MOR, CFI, DON, and SFH. MOR were selective for the formation of 2,6-DIPN even in the isopropylation, and they increased further in the *s*-butylation and *t*-butylation with the increase in the bulkiness of alkylating agents. The bulkiness of alkylating agents also enhanced the 2,6-selectivities over the 14-MR zeolites. The 2,6-selectivities were much improved up to 50–60% in the *s*-butylation, and they were further improved in the *t*-butylation: 90% for CFI and 80% over DON and SFH. From these results, it is summarized that high *β*,*β*- and 2,6-selectivities are obtained in the channels of the 14-MR zeolite by the steric interaction by bulky alkylating agents.

The features of the *β*,*β*-selectivities and the 2,6-selectivities over one-dimensional 14-MR zeolites, CFI, DON, and SFH, are different from those over one-dimensional 12-MR zeolites, MOR, AFI, ATS, and IFR,[16] and three-dimensional zeolites, FAU, BEA, and CON as reported in previous work.[17]

MOR and AFI gave high *β*,*β*-selectivities in all alkylations, by using propene, 1-butene, and 2-methylpropene. However, the *β*,*β*-selectivities over ATS and IFR were increased with increasing bulkiness of alkylating agent: 40% for the isopropylation, 80% for the *s*-butylation, and almost 100% for the *t*-butylation. The *β*,*β*-selectivities over FAU, BEA, and CON also increased with increasing the bulkiness of alkylating agents:

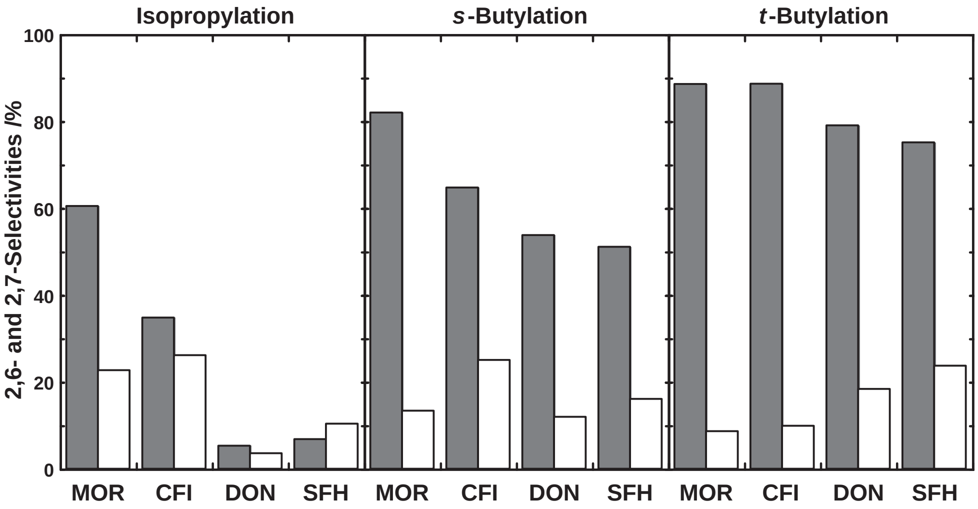

Figure 8. The 2,6- and 2,7-selectivities in the alkylation of NP over the zeolites. Reaction conditions: see Figure 7. Legends: ■: 2,6-DAN; □: 2,7-DAN.

30–40% in the isopropylation, 75–85% in the *s*-butylation, and higher than 95% in the *t*-butylation, respectively. These differences in the β,β-selectivities are due to synergistic effects of zeolite channels and bulkiness of alkylating agents as discussed in previous sections. The precise fitting of the transition state in the channels is essential for the high β,β-selectivities. The low β,β-selectivities are due to kinetic and thermodynamic controls because the reaction space is large enough to allow the formation of bulky isomers.

The 2,6-selectivites in the isopropylation were as high as 60% and 50% over MOR and AFI, respectively at 250 °C; however, they were as high as around 20% over ATS and IFR. The 2,6-selectivities were as high as 15–25% in the isopropylation over FAU, BEA, and CON. The channels of these zeolites are too large for recognizing the difference between 2,6- and 2,7-DIPN. However, the increase in bulkiness of alkylating agent enhanced the 2,6-selectivities over all zeolites including ATS, IFR, DON, and SFH in the *s*-butylation and *t*-butylation. On the other hand, over FAU, BEA, and CON the increase in the bulkiness of alkylating agent improved both 2,6- and 2,7-selectivities because of the increase in the β,β-selectivities: the ratio of 2,7-/2,6-DAN remained low even by using bulky alkylating agent. Particularly, FAU gave predominantly 2,6-DTBN; however, BEA and CON gave almost equimolar mixtures of 2,6- and 2,7-DTBN although β,β-DTBN was formed exclusively: these features are different from one-dimensional 12- and 14-MR zeolites. Although they can recognize the differences in β,β-DTBN and the other isomers, the channels of FAU, BEA, and CON are too large for the discrimination of 2,6- and 2,7-DAN, and thermodynamic control should partly operate at higher temperatures.

From the results of the alkylation of NP over various zeolites, it is concluded that β,β-DAN can be differentiated from bulky isomers over zeolites with large reaction spaces in the channels if bulky alkenes are used as alkylating agent, and that the 2,6-selectivities appear by the discrimination of small differences in steric interaction among DAN isomers with zeolite channels.

In previous papers, we found an increase in the selectivities for 4,4′-dialkylbiphenyl (4,4′-DABP) with the increase in the bulkiness of alkylating agent in the alkylation of BP over one-dimensional 14-MR zeolites, CFI, DON, and SFH,[27] over one-dimensional 12-MR zeolites, MOR, AFI, ATS, and IFR,[30] and over three-dimensional 12-MR zeolites, FAU, BEA, and CON.[31] High selectivities for 4,4′-DABP originate from the discrimination of 4,4′-DABP from other isomers, particularly from 3,4′-DABP, at transition states. However, the difference between 2,6- and 2,7-DAN was small compared to the difference between 4,4′- and 3,4′-DABP in the alkylation of BP.

In summary, the results discussed on the alkylation of NP and BP over the zeolites indicate that the β,β- and 2,6-selectivities for DAN isomers and 4,4′-selectivities for DABP isomers are synergistically governed by the type of zeolite channels and bulkiness of alkylating agents.

Conclusion

The selectivities for dialkylnaphthalene (DAN) isomers in the alkylation, i.e., isopropylation, *s*-butylation, and *t*-butylation of naphthalene (NP) was studied over one-dimensional 14-MR zeolites, CIT-5 (CFI), UTD-1 (DON), and SSZ-53 (SFH), and compared to those over MOR. Two types of selectivity, β,β- and 2,6-selectivities were observed in the alkylation of NP. These selectivities varied with the types of zeolite and alkylating agent.

The β,β-selectivities, which are due to the discrimination of β,β-DAN from their 12 isomers, were higher than 90% in the isopropylation over MOR; however, those over CFI, DON, and SFH were much lower than those over MOR: predominant isomers over the 14-MR zeolites were bulky and less stable α,β-DIPN (1,3-, 1,5-, and 1,7-DIPN) and α,α-DIPN (1,4- and 1,5-DIPN) at low temperatures, and the formation of stable β,β-DIPN (2,6- and 2,7-DIPN) increased with increasing temperature. The β,β-selectivities were higher than 95% in the *s*-butylation over MOR and CFI. They were lower for DON and SFH although they increased with an increase in temperature. The *t*-butylation gave almost 100% β,β-selectivities over all zeolites. These results suggest the increase in the bulkiness of alkylating agents enhances steric restriction even over the zeolites with large reaction space, resulting in enhancing the β,β-selectivities. Thermodynamic control also possibly participates in higher temperatures to increase the β,β-selectivities.

The 2,6-selectivities, which are due to the discrimination of 2,6-DAN from other isomers, particularly between 2,6- and 2,7-DAN, increased by using bulkier alkylating agents. They are higher than 60% in the isopropylation over MOR at moderate temperatures below 275 °C. Low 2,6-selectivities over CFI, DON, and SFH were observed in the isopropylation; however, they were enhanced in the *s*- and *t*-butylations.

These different features among zeolites are explained by the discrimination of the least bulky isomers from other bulky isomers at transition states by steric restriction with the zeolite, where the difference in pore-entrance and channel structures cause the difference in the isomers: β,β-DAN from the DAN isomers; and 2,6-DAN from β,β-DAN. The bulkiness of alkylating agent also enhances the discrimination of the isomers, particularly, between 2,6- and 2,7-DAN. The β,β- and 2,6-selectivities are synergistically governed by the zeolite channel and the bulkiness of alkylating agents.

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Supporting Information

Figures S1–S6: The influence of reaction temperature on the yields of alkylates in the alkylation of NP. Figure S7: Models of pore-entrances and channels of MOR, CFI, DON, and SFH topologies. This material is available free of charge on the Web at: http://www.csj.jp/journals/bcsj/.

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